

Vapor Pressure of Organic Solutions

And Application of Dühring's Rule to Calculation of Equilibrium Diagrams

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Vapor Pressure of Organic Solutions¹

And Application of Dühring's Rule to Calculation of Equilibrium Diagrams

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THE design and construction of efficient apparatus for evaporation and distillation should be based on exact knowledge of the properties of the substance or solution to be handled. Yet to one who seeks the necessary vapor pressure data and equilibrium diagrams, the fact is soon apparent that the literature affords scanty information and that such data as are available are frequently discordant. This is particularly true of organic liquids and solutions. For this reason the writers decided to study the vapor pressure relationships of a number of organic substances in the hope of making useful data available and of simplifying methods for establishing complete information regarding vapor pressure and equilibrium diagrams.

Numerous equations have been proposed to express the relationship between the pressure and temperature of saturated vapors. Many of these are empirical, although a few are partly in rational form. Among the more frequently used equations are those of Biot

$$\log p = a + bA^t + cB^t$$

in which a , b , c , A , and B are constants for a particular substance; of Rankine, as modified by Kirchoff and Dupre,

$$\log p = A - \frac{B}{T} + C \log T$$

in which A , B , and C are constants for a particular substance, and of Bertrand

$$\log p = \log K - n \log \left(\frac{T}{T-b} \right)$$

in which k , n , and b are constants for a particular substance.

Each of these equations involves several constants, and therefore requires at least as many experimental determinations as there are constants in the equation. Preferably, other experimentally determined values should be known in order to determine the values of the constants more accurately. These equations are useful as a means of interpolation between known points on the vapor pressure curve, but a large number of calculations must be made in order to establish the curve completely.

In 1878, Dühring² discovered a simple relation between the boiling points of pure substances. He plotted the boiling point of a pure substance at a given pressure as the ordinate against the boiling point of water at the same pressure as the abscissa. Repeating this process for several widely different pressures, he showed that a straight line could be drawn through all the points thus determined. This conclusion was reached from a study of about fifty pure substances whose chemical and physical properties differed greatly. Dühring expressed the relationship algebraically:

$$\frac{T_1 - T_2}{\Theta_1 - \Theta_2} = K$$

in which T_1 and T_2 are the boiling points of one substance at two different pressures, Θ_1 and Θ_2 the boiling points of the other substances at the same two pressures, and K a constant that is the slope of the line.

Dühring's rule has been shown to hold remarkably well for single substances over limited ranges of pressure, particularly when the boiling

points of the substance whose vapor pressures are in question are plotted against the known boiling points of a chemically similar substance. Over pressure ranges of several thousand millimeters there may be deviations ranging from nothing up to 10 or 15 per cent in the slopes of the Dühring curve. In general, the broader the range pressure, and the less similar the sub-

stances, the greater the deviation of the curve from a straight line. Table I presents data illustrative of the constancy of the Dühring K for substances of several types. A slight change in the direction of a curve results in a relatively large change in the value of the slope. Unless the sensitiveness of the tangent as a criterion is held in mind, one will be overly impressed as regards the actual error in temperature readings made from the Dühring lines.

The deviation of curves based on Dühring's rule from curves determined by experiment is shown in Figure 1. The solid lines are the Dühring lines. The broken lines are drawn through the points representing experimental values. The solid and broken lines for ethyl alcohol are coincident throughout their length and for the other substances are coincident below atmospheric pressure.

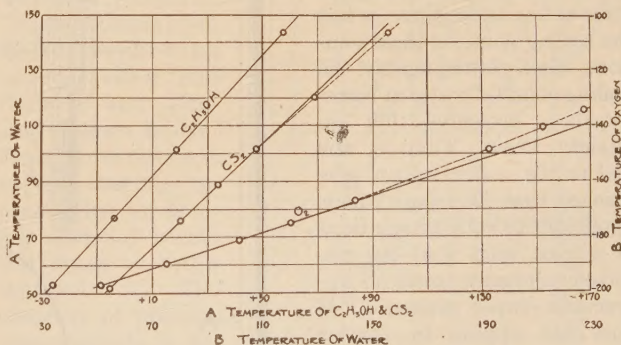


Figure 1—Dühring Lines for Ethyl Alcohol, Carbon Disulfide, and Oxygen

(Use coordinates A for alcohol and carbon disulfide and B for oxygen)

Ramsay and Young³ also formulated an expression relating the boiling points of pure substance. This may be written

¹ Received March 16, 1925.

² "Neue Grundgesetze zur Rationelle Physik und Chemie," Leipzig, 1878.

³ Phil. Mag., [5] 20, 515 (1885); 21, 33 (1886); 22, 37 (1886).

Table I—Values of Slope (K) of Dühring Curves
(Water is the reference substance)

OXYGEN ^a		ETHYL ALCOHOL ^b		ACETIC ACID ^c		CHLOROFORM ^b		CARBON DISULFIDE ^b		HEXANE ^d	
Pressure Mm.	K	Pressure Mm.	K	Pressure Mm.	K	Pressure Mm.	K	Pressure Mm.	K	Pressure Mm.	K
100-300	3.15	100-300	1.085	100-300	0.873	200-500	0.966	100-300	0.945	120-185	0.938
300-800	3.15	300-800	1.110	300-700	0.850	500-800	0.926	300-500	0.932	185-277	0.931
800-1500	2.98	800-3000	1.110	700-1040	0.836	800-1500	0.925	500-800	0.918	277-401	0.903
1500-3000	2.92	3000-5000	1.095			1500-3000	0.893	800-1500	0.890	401-566	0.899
3000-5000	2.73	5000-10000	1.101			3000-5000	0.844	1500-3000	0.800	566-787	0.902
5000-10000	2.62	10000-15000	1.101			5000-8000	0.830	3000-5000	0.842	787-1407	0.863
10000-15000	2.51	15000-20000	1.107							1407-2982	0.839
15000-20000	2.39									2982-6793	0.803
										6793-11380	0.775
										11380-15577	0.773

^a Olzewski and Wroblewski recalculated by Ramsay and Young, *Phil. Mag.*, [5] **21**, 42 (1886).^b Ramsay and Young, *Ibid.*, [5] **20**, 524 (1885).^c Ramsay and Young, *J. Chem. Soc. (London)*, **49**, 805 (1886).^d Ramsay and Young, *Proc. Roy. Soc. (London)*, **12**, 389 (1909-10).

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} = \text{a constant}$$

that is, the ratio of the absolute temperatures at which two substances boil under the same pressure is a constant. This equation is generally not so accurate as Dühring's, and is less desirable in that the constant is not the slope of the line. If a third term is added so that

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} + C(T_B - T'_B)$$

the equation is found to represent experimental data more accurately than the simpler form or than Dühring's rule. However, the addition of the third term changes the equation to one of the second degree.

The generalization of Dühring's rule is as accurate as most of the data on vapor pressures recorded in the literature. It holds closely for pressures below atmospheric and is sufficiently accurate for engineering purposes even up to pressures of 10 to 20 atmospheres. At pressures of an atmosphere or less the deviations from Dühring's rule are so small that in all but the most precise scientific work this law will express the data within the limits of experimental error.

Curiously enough, as had been noted by Baker and Waite,⁴ Dühring's rule had never been applied to aqueous solutions. These investigators studied binary solutions of inorganic substances in water, and demonstrated that at pressures of one atmosphere or less the boiling points of these solutions, when plotted against the boiling points of water at corresponding pressures, fell on straight lines. That is, the valuable conclusion was reached that Dühring's rule is applicable to aqueous solutions of a type such that the dissolved substance exerts no appreciable vapor pressure. It does not appear to matter whether the concentration of these solutions is high or low, whether the salt is highly ionized or not, or whether the solute is one that is hydrated in solution.

⁴ *Chem. Met. Eng.*, **25**, 1137 (1921).

With the fundamentally important conclusions of Baker and Waite in mind, the next logical step was to investigate Dühring's rule in relation to solutions of organic liquids. Here both solute and solvent exert appreciable vapor pressures, and the concentration of either or any component may be nearly zero or almost unity.

The writers' experiments have shown that Dühring's rule is applicable to solutions of hydrocarbons. Study of data from the literature presented in a later section of this paper confirms the conclusion that Dühring's rule is applicable in general to solutions any or all of whose components exert appreciable vapor pressures. This applies to all binary and ternary solutions whose vapor pressure data have been studied.

Experimental

Apparatus and Methods

The apparatus (Figure 2) is similar to that of Baker and Waite.⁵ The solution whose vapor pressure was to be determined was placed in a glass tube, *I*, and heated by passing an electric current through the resistance coils in the heater *C*. The current was regulated by means of an external resistance and the amperage and voltage read. A modified Cottrell tube, *D*, was slipped over the heater and used for pumping a mixture of the solution and vapor over the bulb of the platinum resistance thermometer, *B*. The tube *I* was closed by the ground glass joint *N*, and jacketed by a second glass tube (not shown in Figure 2). Thus the effect of air currents was minimized. The vapors coming from the boiling solution passed into a condenser, *G*, connected to the large glass reservoir *H*. From *H* a glass tube led to a small catch bottle, *J*, connected to a vacuum pump. The catch bottle was also connected to a vacuum regulator consisting of two parts, a manometer *M* and a needle valve operated by the solenoid *K*. A decrease in pressure below the value desired would cause the mercury to rise in the manometer and in turn to make contact with the platinum-tipped rod, *F*, thus completing a low-voltage circuit through the solenoid, *K*, and raising the armature. The lower end of the solenoid armature was the plug of the needle valve that regulated the inlet of air.

It was necessary to be able to regulate the lift of the needle valve, since different openings were required for best pressure

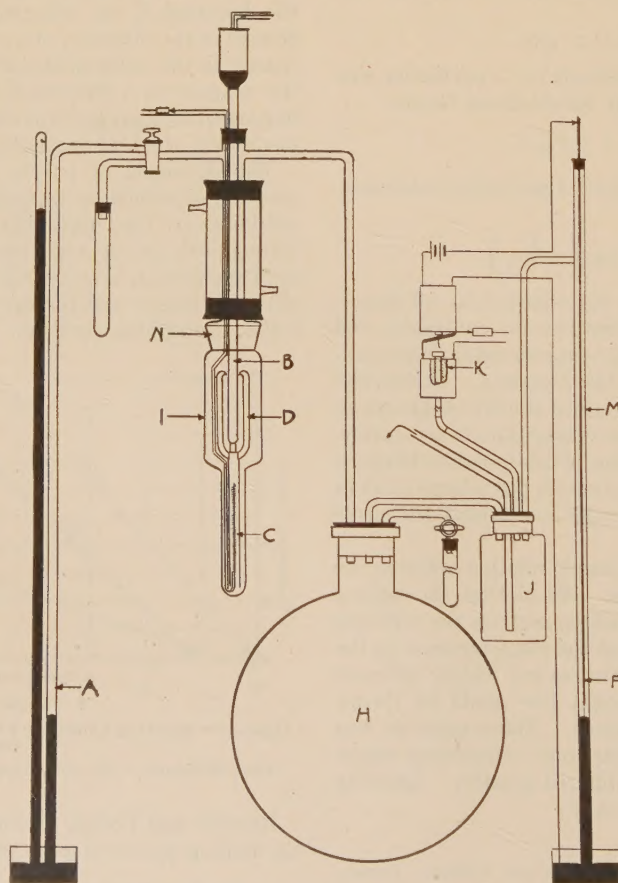
⁵ *Trans. Am. Inst. Chem. Eng.*, **13**, Pt. 2 (1920).

Figure 2—Diagram of Apparatus

control at different absolute pressures. This regulation was obtained by screwing the upper end of the solenoid core up or down to the required position. By a proper setting of the pump the pressure was regulated to a value slightly below that wanted, and the "vacuum regulator" adjusted to give the vacuum desired. The mercury in the regulating manometer oscillated regularly, but the reservoir *H* served to damp these oscillations and to maintain a constant vacuum in the boiling point apparatus. This vacuum was measured by a manometer, *A*, connected directly to the boiling point tube, thus insuring that the pressure read was the true pressure under which the liquid was boiling. To minimize the effect of capillary action, the manometer was made of 10-mm. glass tubing. The variations in pressure in the boiling point tube were so slight that the bottom of the mercury meniscus in the measuring manometer showed no perceptible movement over periods as long as half an hour, but the center of the meniscus would regularly breathe or oscillate up and down a distance of 0.05 to 1.0 mm. from a mean position. The measuring manometer was mounted before a mirror to aid in eliminating parallax in reading, and beside a graduated steel rule adjusted so that its lower end was just level with the center of the mercury meniscus in the low arm and the graduated edge of the rule next to the center line of the mercury in the high arm. The reading of the center of the meniscus in the high arm was taken with the aid of a magnifying glass.

A 10-mm. tube filled with mercury was hung beside the measuring manometer and its temperature read on a mercury thermometer whose bulb extended some distance into this mercury. The temperature so read was taken as the temperature of the mercury in the measuring manometer. By this means the effect of thermometric lag in reading barometer temperatures was eliminated.

The temperature of the boiling solution was taken by means of a platinum resistance thermometer, *B*. This thermometer was not immersed in the body of the liquid, but was in the vapor space. The thermometer tube was kept well wetted with solution for a distance about an inch above the platinum coil by means of the pumping tube *D*. The resistance thermometer was a Leeds and Northrup bulb, constructed according to the method given by the U. S. Bureau of Standards,⁶ and provided with compensating leads. The resistance was measured by means of a Leeds and Northrup dial bridge and deflecting galvanometer. A commutator was used in connection with the bridge to reverse the direction of current through its arms, thus eliminating any error resulting from change of resistance of the arms of the bridge. One of the three leads to the thermometer was connected in the battery circuit, and the other leads were placed one in each of the arms of the bridge. The pressure measured by the manometer *A* was independent of atmospheric pressure changes, so no barometer readings were necessary in obtaining the absolute pressure.

Errors in Measurements

The sources of error in boiling point determinations have been so completely discussed by Smith and Menzies⁷ and others that only those peculiar to this apparatus will be mentioned.

Use of the vacuum regulator made it possible to maintain a constant mean difference between barometric pressure and the pressure in the apparatus for as long a period as was desired. In a few determinations the pressure in the apparatus actually oscillated as much as ± 1.5 mm. from the mean value, but as these oscillations were rapid and regular, it may be safely assumed that their effect on the mean boiling point of the solution was nil.

The platinum thermometer was calibrated at the temperature of melting ice, at the normal boiling point of water, and at the normal boiling point of sulfur. From the readings thus obtained, the values of the constants in the formula $R_t = R_o (1 + at + Bt^2)$ were determined. A calibration curve was then constructed using a scale such that 1 mm. corresponded to 0.1°C . The temperatures recorded for the boiling points of the solutions at various pressures are believed to be accurate to $\pm 0.05^\circ \text{C}$. The sensitivity of the temperature-measuring equipment was 0.001°C . However, difficulties in maintaining constant conditions during the time required for an observation were such that the error in the

recorded temperatures may be as much as $\pm 0.05^\circ \text{C}$. The absolute pressures as measured by the mercury manometer *A* were reduced to equivalent readings at 0°C . The steel rule was compared with other standards and found to be accurate to within less than 0.1 mm. at 25°C . The heights of the mercury columns could be read as accurately as a mercury barometer. The mercury used had been purified with nitric acid, followed by a double distillation *in vacuo*.

Each hydrocarbon used in the work distilled within a range of 0.1°C . of the true boiling point at the particular pressure. As a check on the purity of each hydrocarbon, one-half of the entire quantity of the substance was separated from the other half by vacuum distillation. No widening of the boiling range was observed, as would have been noted if the material was a constant-boiling mixture of two or more substances. The properties of the portion separated as distillate, and of the residue in the flask, were identical within the limits of error already given. Any dissolved gases were completely swept out of the apparatus during the 30-minute period of ebullition allowed for the system to come to equilibrium in making each boiling point determination.

Superheating of the liquid was impossible, first, because the heat was conducted to the solution directly by the immersed heating coils, and second, because the solution that came in contact with the thermometer had been pumped by its own vapor onto the thermometer, thus allowing time and the intimacy of contact required for the vapor and liquid to come into equilibrium with each other. It is obvious that the boiling points as determined were not altered as a result of an hydrostatic head of boiling liquid.

Table II—Comparison of Boiling Points of Water at Various Pressures with Values Obtained By Holborn and Henning

Pressure as read Mm.	Temp. of manometer as read $^\circ \text{C}$.	Corr. absolute pressure Mm.	Temp. obsd. $^\circ \text{C}$.	Temp. from steam tables H. & H. $^\circ \text{C}$.	Diff. $^\circ \text{C}$.
654.5	27	651.2	95.70	95.72	0.02
612.0	26	609.0	93.88	93.91	0.03
402.0	21	400.4	82.97	82.99	0.02
350.0	27	348.2	79.49	79.52	0.03
205.5	27.5	204.5	66.95	66.95	0.00
148.0	27.5	147.23	59.68	59.71	0.03

To test the accuracy of the entire apparatus, determinations of the boiling point of water, at pressures such that the boiling range was 50° to 100°C ., were made. These results are shown in Table II. The fifth column gives the corresponding values taken from Holborn and Henning's steam tables.⁸ From these results it appears that the apparatus has an absolute accuracy within this range of better than $\pm 0.05^\circ \text{C}$. The accuracy of pressure measurements is believed to be well within ± 1.5 mm. For example, an error of 1.5 mm. in reading the pressure at 120 mm. would mean an error of 0.05°C .

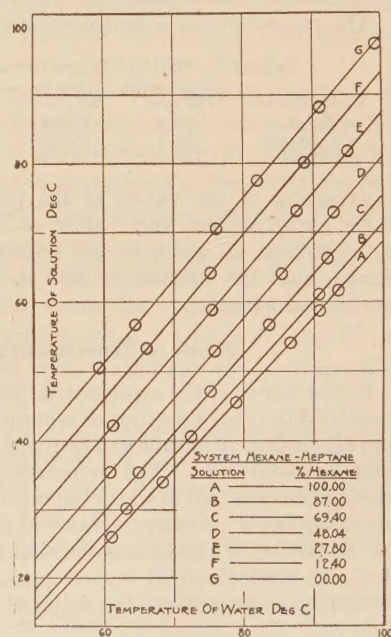


Figure 3—Dühring Lines for the System Hexane-Heptane

⁶ Bur. Standards, Sci. Paper 407.

⁷ J. Am. Chem. Soc., 32, 1412 (1910).

⁸ Ann. phys., [4] 26, 833 (1908).

Preparation of the Hydrocarbons

The *n*-hexane, *n*-heptane, and *n*-octane used in this investigation were separated from a paraffin-base naphtha derived from Kanawha County, W. Va., petroleum.⁹ The isolation of the individual hydrocarbons was effected by a process of

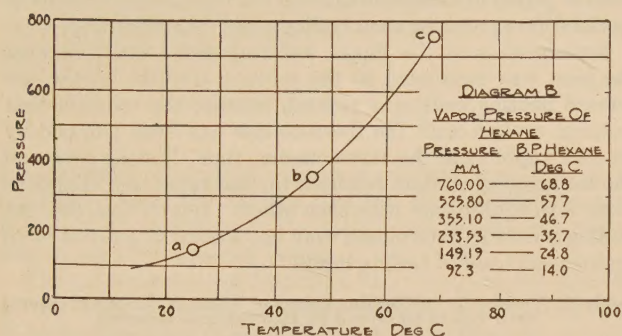
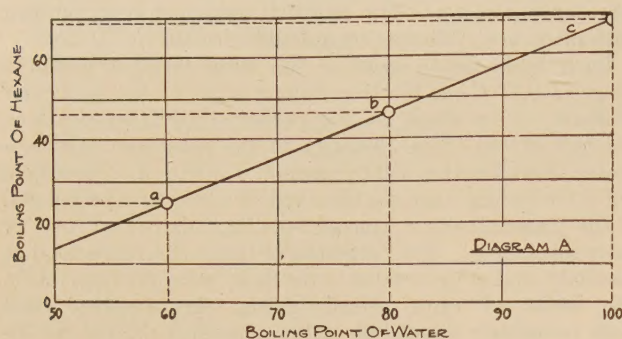


Figure 4
Diagram A—Dühring Line for Hexane
Diagram B—Vapor Pressure Curve for Hexane as Calculated from Diagram A

careful fractional distillation. The actual operations will be described in a later paper on the composition of this particular naphtha. Quantities of 300 to 400 cc. of each hydrocarbon were available for experimental work.

The properties of the hydrocarbons are given in Table III.

Table III—Physical Properties of Hydrocarbons

HYDROCARBON	Boiling point 760 mm.	Sp. gr. 20°/20° C.	Refractive index	
			20° C.	25° C.
<i>n</i> -Hexane	68.8	0.6622	1.3851	1.3840
<i>n</i> -Heptane	98.7	0.6893	1.4068	1.4058
<i>n</i> -Octane	124.3	0.7123	1.4059	1.4037

Comparison of the values of the physical properties of the three hydrocarbons with values of the properties of other hydrocarbons as given in the literature leads to the conclusion that the substances used in this investigation were the normal paraffins.

Scope of Experimental Work

In the course of the experimental work, measurements were made of the vapor pressures of *n*-hexane, *n*-heptane, *n*-octane, and of solutions of hexane and heptane, hexane and octane, and heptane and octane. The temperature range investigated for each system was that in which the substance or solution showed the same vapor pressure as water in the temperature interval 50° to 100° C. The boiling point of each substance or solution was determined at several pressures, although, as will be seen, only two points are required to establish a Dühring line.

Figure 3 represents the results of a study of the system hexane-heptane with the object of determining the validity of the generalization of Dühring's rule. The lines are drawn

⁹ This naphtha was furnished by the Elk Refining Co., of Charleston, W. Va., to whom the writers are indebted for this material assistance.

as straight lines. The points representing the experimental data in no case fall as much as 0.1° C. off the lines. Similar figures might be given to cover the systems hexane-octane and heptane-octane, data for both of which were determined experimentally and are presented in Table IV.

Confirmation of Dühring's Rule from Experimental Data

The first conclusion that can be drawn from the experimental work is that Dühring's rule holds for these solutions, each component of which exerts an appreciable vapor pressure. Dühring's rule has heretofore been recognized as applicable to pure substances, or to solutions from which the solvent alone was volatile. Its extension to solutions of volatile liquids greatly simplifies the establishment of total vapor pressure curves for such solutions.

After the accuracy of the generalization for these hydrocarbons had been determined, a search of the literature brought to light many other confirmative data that will be discussed later.

Use of Dühring Lines in Constructing Vapor Pressure Curves

When the Dühring line of a pure substance is known the vapor pressure curve can be readily drawn. This is illustrated in Figure 4. Diagram A shows the Dühring line for hexane. The ordinates are the boiling points of hexane and the abscissas are the boiling points of water. The vapor pressure data can be read from this chart in the following manner:

Choose any water temperature—for example, 60° C. This represents a pressure of 149.19 mm. Follow the vertical dotted line to the Dühring line at point *a* and then the horizontal dotted line to the vertical axis and read the temperature of the boiling point of hexane, in this case 24.8° C., which corresponds to the vapor pressure 149.19 mm. This gives one point on the vapor pressure curve for hexane. Repeat the process at small differences in water temperature and the data necessary for the construction of the vapor pressure curve for hexane are obtained. These data are plotted in Diagram B of Figure 4.

The chief advantage of this method of constructing vapor pressure curves lies in the fact that only two points are required to establish the Dühring line, whereas previously it has been necessary to make a large number of determinations of vapor pressure in order to draw the vapor pressure

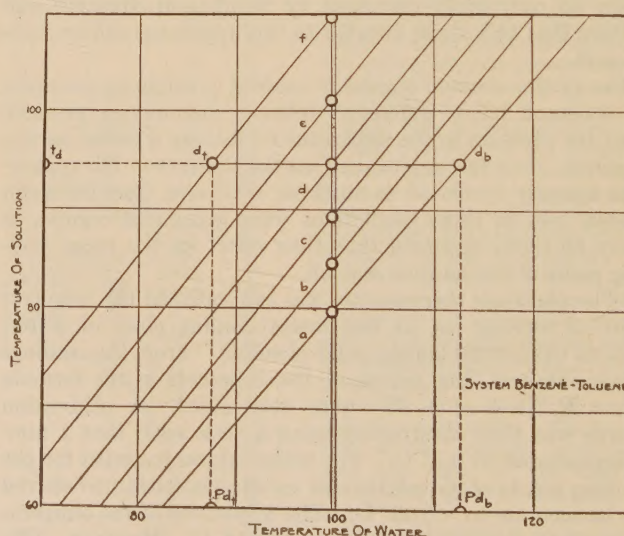


Figure 5—Dühring Lines for the System Benzene-Toluene

curve accurately. In precise work three or more boiling points would be determined in order to be sure of the exact slope of the Dühring line, but in no case would the required

Table IV—Boiling Points (° C.) of Solutions

Pressure Mm.	Boiling point of water ° C.	Hexane 100% Octane 0%										Hexane 0% Octane 100%	
		90	80	70	60	50	40	30	20	10	90	90	100%
760.0	100	68.8	71.6	74.9	78.4	82.6	87.1	92.3	97.2	105.9	115.2	124.3	
525.8	90	57.7	60.3	63.4	66.9	71.0	75.7	80.7	85.8	94.0	102.6	117.7	
355.1	80	46.7	49.0	51.8	55.4	59.4	64.0	69.0	74.3	82.0	89.9	99.2	
233.53	70	35.7	37.7	40.4	43.8	47.8	52.5	57.5	62.7	70.1	77.2	86.6	
149.19	60	24.8	26.5	28.9	32.4	36.2	40.8	45.9	51.4	58.2	64.6	74.2	
92.30	50	14.0	15.2	17.6	20.9	24.7	29.2	34.3	40.0	46.3	51.9	61.8	

Pressure Mm.	Boiling point of water ° C.	Hexane 100% Heptane 0%										Hexane 0% Heptane 100%	
		90	80	70	60	50	40	30	20	10	90	90	100%
760.0	100	68.0	70.8	72.8	75.1	77.5	80.2	83.3	86.6	90.2	94.2	98.6	
525.8	90	57.7	59.5	61.5	63.7	66.0	68.6	71.7	74.8	78.4	82.4	86.6	
355.10	80	46.7	48.4	50.2	52.4	54.5	57.0	60.0	63.2	66.7	70.7	74.8	
233.53	70	35.7	37.4	39.0	40.9	43.0	45.5	48.4	51.5	54.9	58.8	63.9	
149.19	60	24.8	26.2	27.8	29.7	31.6	34.0	36.7	40.0	43.4	47.1	51.2	
92.30	50	14.0	15.2	16.6	18.3	20.2	22.5	25.2	28.3	31.7	35.4	39.5	

Pressure Mm.	Boiling point of water ° C.	Heptane 100% Octane 0%										Heptane 0% Octane 100%	
		90	80	70	60	50	40	30	20	10	90	90	100%
760.0	100	98.70	100.4	102.2	104.0	106.0	108.3	111.2	114.3	117.5	120.8	124.3	
525.8	90	86.60	88.4	90.2	92.0	93.8	96.1	99.0	102.1	105.2	108.4	111.7	
355.10	80	74.80	76.5	78.2	80.0	81.8	84.0	86.8	89.8	92.8	95.8	99.2	
233.53	70	63.90	64.6	66.1	68.1	69.9	72.0	74.6	77.4	80.4	83.6	86.6	
149.19	60	51.20	52.7	54.1	56.0	57.8	60.0	62.5	65.2	68.1	71.1	74.2	
92.30	50	39.50	40.7	42.2	43.9	45.8	48.0	50.4	53.0	55.8	58.7	61.8	

experimental work be as laborious as that necessary to locate the vapor pressure curve itself.

Table IV presents vapor pressure data for hexane, heptane, and octane and for the binary solutions of hexane and heptane, hexane and octane, and heptane and octane as determined in the course of the experimental work.

Construction of Equilibrium Diagrams from Dühring Lines

When a family of Dühring lines has been established for a binary system, it becomes possible to construct isobaric and isothermal equilibrium diagrams for the system. This is of great importance, because equilibrium diagrams, in addition to defining the systems under all conditions, are the basis of the design of equipment for fractional distillation. A simple and rapid method for constructing them is much to be desired.

In practice, isobaric diagrams are of far more importance than isothermal diagrams, because distillation, or vaporization in general, is conducted at constant pressure rather than at

shown in Figure 5. Suppose that the isobaric diagram for 750 mm. pressure is required. Draw a line perpendicular to the horizontal axis at the point representing a temperature of 99.62° C.—that is, at the point corresponding to the temperature at which water boils under 750 mm. pressure. This line intersects the Dühring lines at points *a*, *b*, *c*, *d*, *e*, and *f*. Consider any one of the solutions for which a Dühring line is known—for example, the solution in which the mol fraction of benzene, in the liquid, is 0.40. The perpendicular intersects this line at point *d*. Through *d* draw a line parallel to the horizontal axis. This line cuts the Dühring lines for benzene and toluene at points designated as *d_b* and *d_t*, respectively. From each of these points project vertically to the horizontal axis, as indicated by the dotted lines, to determine the points *P_b* and *P_t*. From the temperatures of water at points *P_b* and *P_t*, the corresponding pressures may be determined, which represent the vapor pressures that benzene and toluene would exert if at the temperature *t_d*, the boiling point of the solution of composition 0.40.

Multiply *P_b*, the vapor pressure of pure benzene at temperature *t_d*, by *X_b*, the mol fraction of benzene in the solution, to obtain a value for the partial pressure of benzene *P_b'*. Further, multiply *P_t* by *X_t* to obtain *P_t'*, the partial pressure of toluene. Subtract *P_t'* from the total pressure, in this instance 750 mm., to obtain a value for the partial pressure of benzene on the vapor that may be designated as *P_b''*. *P_b'* and *P_b''*, the two calculated values for the partial pressure of benzene in the vapor, are not equal. Divide *P_b'* and *P_b''* by the total pressure 750 mm. to obtain the corresponding mol fractions *X_b'* and *X_b''*.

In order to obtain a value for benzene in the vapor that more nearly checks experimental values, multiply *X_b'* by *X_b* and *X_b''* by *X_t* and add the results. The resultant sum is the molar composition in terms of benzene. This subtracted from unity gives the mol fraction of toluene in the vapor.

As an illustrative calculation consider the same solution as described above where the concentration of benzene is 0.40 mol. The point *d*, Figure 5, is at the temperature *t_d* or 94.6° C., the boiling point of the solution. The pressure exerted by benzene, if it were alone at the temperature 94.6° C. represented by the point *P_b*, would be 1178.5 mm. This pressure corresponds to the water temperature at *P_b* or 112.7° C. The pressure exerted by toluene is found in a similar way and is 472.3 mm. Then

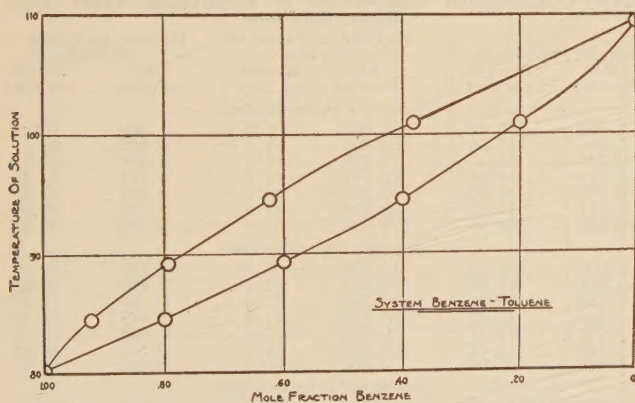


Figure 6—Equilibrium Diagram for System Benzene-Toluene at 750 Mm.

constant temperature. However, as is obvious, when several isobaric diagrams are known, it becomes possible to draw any desired isothermal diagram.

The method of constructing any isobaric diagram is illustrated in Figures 5 and 6. Dühring lines for benzene and toluene are chosen because the equilibrium diagram for this system has been carefully determined experimentally. The Dühring lines for several solutions of these substances are

$P_{d_b} \cdot X_b = 1175.8 \times 0.4 = 470.3 \text{ mm.} = P'_B$ the partial pressure of benzene

$P_{d_t} \cdot X_t = 472.3 \times 0.6 = 283.4 \text{ mm.} = P'_T$ the partial pressure of toluene

$$750 - 283.4 = 466.6 \text{ mm.} = P''_B$$

$$\frac{470.3}{750} = 0.628 = X'_B$$

$$\frac{466.6}{750} = 0.622 = X''_B$$

$$X'_B \cdot X_B = 0.628 \times 0.4 = 0.251$$

$$X''_B \cdot X_T = 0.622 \times 0.6 = 0.373$$

0.624 mol benzene in the vapor

1.000 - 0.624 = 0.376 mol toluene in the vapor

Similar calculations are made for the other solutions of benzene and toluene and since the boiling points for each solution are known, the isobaric equilibrium diagram may be constructed as shown in Figure 6.

Although the description of this procedure is somewhat lengthy, the operation is simple. The method is based on Raoult's law, remembering that this law states that the partial pressure of the solvent from a solution is equal to the product of the vapor pressure of the solvent at the temperature of the solution and the mol fraction of the solvent in the solution. Raoult's law, as such, is applicable only to dilute solutions—that is, to solutions containing less than 0.1 mol of solute.

Values for the partial pressures of benzene and toluene, P'_B and P'_T , have been calculated based on the assumption that Raoult's law holds for all concentrations. This assumption is incorrect, but the values so obtained can be used. The partial pressure of benzene from any solution of benzene and toluene may also be calculated by subtracting the partial pressure of toluene, found as above, from the total pressure. That is, $P''_B = P - P'_T$. P'_B and P''_B are not equal. If the actual partial pressure of benzene, P_B , be considered as the sum of two pressures, one of benzene behaving as if alone and the other of benzene determined in a manner such as to

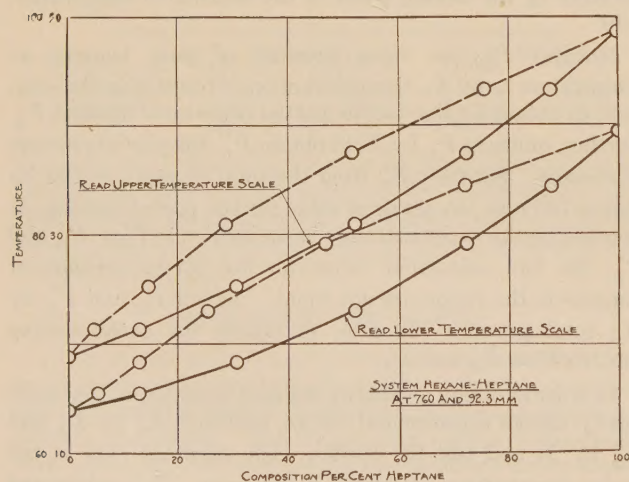


Figure 7—Equilibrium Diagrams for System Hexane-Heptane. The Upper Diagram Is for 760 Mm. and the Lower for 92.3 Mm.

be equivalent to considering toluene as vaporizing alone, the first in proportion to the mol fraction of benzene in the liquid, and the second in proportion to the mol fraction of toluene in the liquid, the value of P_B so calculated will be found to be close to experimentally determined values.

Further discussion of this method for determining the composition of the equilibrium vapor will be presented later.

Equilibrium Diagrams for Systems Hexane-Heptane, Hexane-Octane, and Heptane-Octane

From the vapor pressure data calculations have been made of the composition of the vapors in equilibrium with solutions of three pairs of hydrocarbons studied. The data are shown

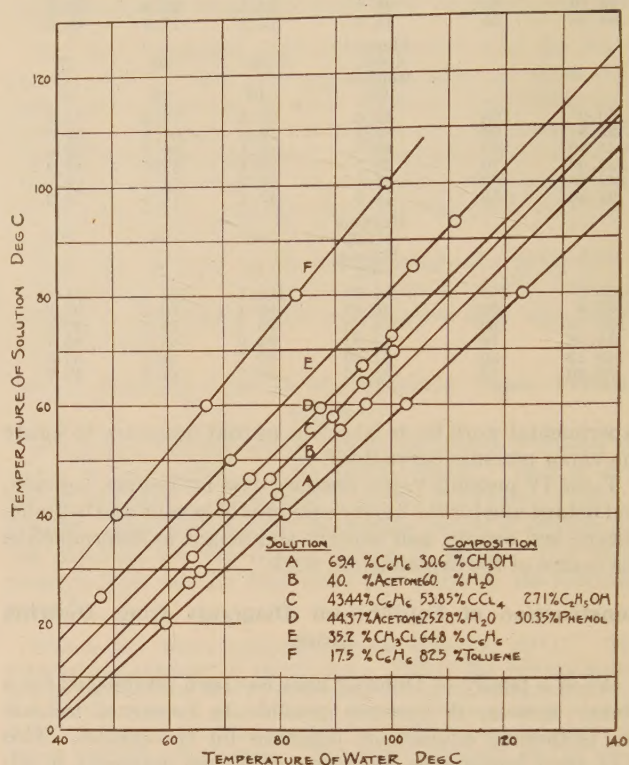


Figure 8—Dühring Lines for Several Organic Solutions

in Table V. Figure 7 shows the equilibrium diagrams for the system hexane-heptane. The upper diagram is that for 760 mm. pressure, and the lower that for 92.3 mm. Similar diagrams may be constructed for the other two systems by using the data given in Table V.

Table V—Calculated Composition of Equilibrium Vapor from Boiling Solutions

HEXANE IN LIQUID	Mol fraction	Weight per cent	HEXANE IN VAPOR AT 760 MM.		HEXANE IN VAPOR AT 92.3 MM.	
			Mol fraction	Weight per cent	Mol fraction	Weight per cent
System: Hexane-Heptane						
1.000	100.00		1.000	100.0	1.000	100.0
0.886	87.00		0.966	95.2	0.952	94.5
0.725	69.40		0.888	87.2	0.886	87.0
0.518	48.04		0.741	71.2	0.773	74.5
0.308	27.80		0.521	48.4	0.569	53.2
0.141	12.40		0.274	24.5	0.312	28.0
0.000	00.00		0.000	00.0	0.000	00.0
System: Hexane-Octane						
1.000	100.00		1.000	100.00	1.000	100.0
0.904	87.61		0.994	98.8	0.989	98.5
0.740	68.22		0.988	97.0	0.963	95.2
0.566	48.70		0.937	91.9	0.913	88.8
0.368	29.77		0.795	77.0	0.810	76.3
0.148	11.57		0.560	48.8	0.550	48.0
0.000	00.00		0.000	00.0	0.000	00.0
System: Heptane-Octane						
1.000	100.00		1.000	100.0	1.000	100.0
0.880	86.6		0.951	94.5	0.948	94.2
0.746	72.0		0.873	85.7	0.883	86.9
0.539	50.60		0.717	68.9	0.752	72.8
0.275	25.00		0.439	40.6	0.480	44.8
0.1095	9.74		0.194	17.9	0.220	19.8
0.0000	0.00		0.000	00.0	0.000	00.0

Calculation of Latent Heats of Vaporization

When the slope of the Dühring line is known for a substance or solution the latent heat may be readily calculated.¹⁰

¹⁰ Walker, Lewis, and McAdams, "Principles of Chemical Engineering," 1923, p. 427. McGraw-Hill Book Company.

This is most fortunate because in addition to equilibrium diagrams, no other information is more likely to be wanted in distillation work than latent heat data.

Analysis of Solutions by Determination of Boiling Point

If the family of Dühring lines is established for any system of components *A* and *B*, an analysis of any solution of these substances is readily made. It is only necessary to determine the boiling point of the solution at some chosen pressure, construct the boiling point-composition curve for the system at this pressure, and from this curve read the composition corresponding to the boiling point of the particular solution.

Determination of Composition of Solution of Maximum or Minimum Boiling Point at Any Pressure

The composition of the binary solution of maximum or minimum boiling point changes with the total pressure. If the Dühring lines for the system are known, it is possible by inspection of these curves to determine the solution of maximum or minimum boiling point at any pressure. To make the method effective, the Dühring lines for a number of solutions whose composition is near that of the solution of maximum or minimum boiling point must be determined. However, the time involved in securing the necessary data is small when one considers that the lines established afford the desired information at all pressures as well as at those at which the boiling point determinations for the establishment of lines were made.

Discussion of Results

Confirmation of Dühring's Rule from Data in Literature

After the accuracy of Dühring's rule for several hydrocarbon solutions had been experimentally demonstrated a thorough search of the literature revealed many confirmatory data.¹¹ Figures 8, 9, and 10 present some of the many Dühr-

¹¹ Schmidt, *Z. physik. Chem.*, **99**, 81 (1921); Schrienemaker, *Ibid.*, **39**, 500 (1902); Konovaloff, *Wied. Ann.*, **14**, 43 (1881); Taylor, *J. Phys. Chem.*, **4**, 363 (1900); Schrienemaker, *Ibid.*, **47**, 447 (1904); Zawidski, *Ibid.*, **35**, 129 (1900); Wreskey, *J. Russ. Chem. Soc.*, **32**, 593 (1900); Carr, unpublished.

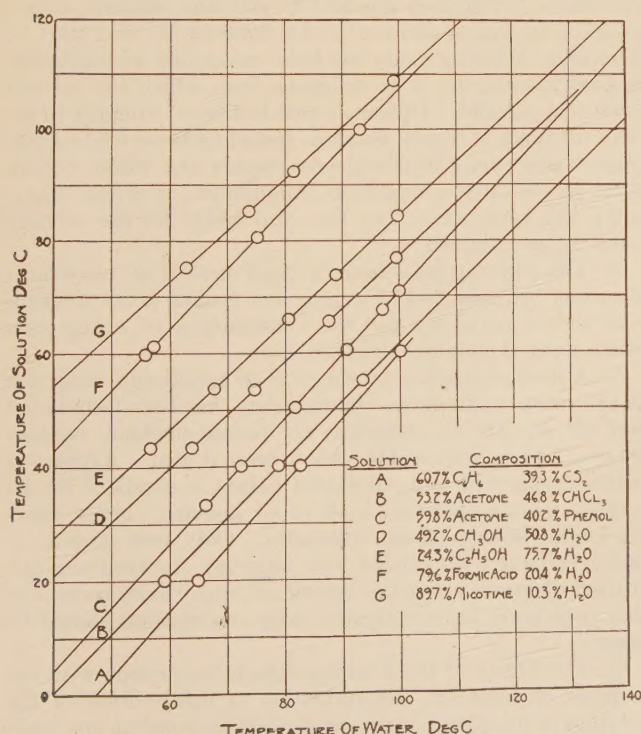


Figure 9—Dühring Lines for Several Organic Solutions

ing lines that can be drawn from data in the literature. These have been selected in such a manner as to include binary systems whose components are partly or completely soluble and whose boiling point curves show a maximum, a minimum, or neither maximum nor minimum. Dühring lines for a few ternary systems are also shown.

Calculation of Equilibrium Diagrams from Data in Literature

The method used for the calculation of equilibrium diagrams from the Dühring lines has already been discussed, with the system benzene-toluene used as an example. The close agreement between calculated and experimental values might be expected, when considering this system, because of the chemical similarity of the components and that, in fact, the application of Raoult's law as such gives a close approximation to the truth in this instance. It is found, however, that the method outlined is applicable to systems whose components are chemically dissimilar, and with a fair degree of accuracy to systems whose boiling point-composition curve shows a maximum or minimum. Raoult's law as such does not afford even an approximation to the truth in these instances.

The application of the method as outlined to systems whose boiling point curves show a maximum or minimum require further explanation. The equilibrium diagram for such a system may be considered as two separate simple diagrams. In Figure 11 these are the portions on either side of line *MN*. The problem is thus resolved into one of calculating vapor composition for one system composed of *A* and constant-boiling mixture, and another composed of *B* and constant-boiling mixture. The method of calculation as previously outlined is applicable to each of these systems.

It may be suggested that the composition of the constant-boiling mixture is a function of the total pressure, and that the method of calculation given above would be difficult to apply over a range of pressure. However, as has been shown, if the Dühring lines are known, the composition of the mixture of maximum or minimum boiling point is easily determined, and thus all difficulty avoided.

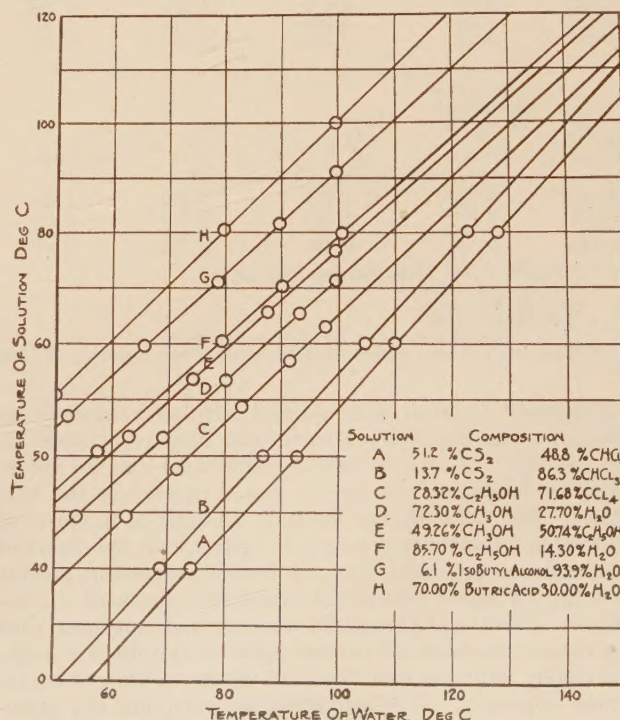


Figure 10—Dühring Lines for Several Organic Solutions

Table VI shows the close agreement between observed and calculated values of vapor compositions for the systems benzene-toluene, carbon disulfide-carbon tetrachloride, carbon tetrachloride-benzene, acetone-chloroform, and alcohol-water. Columns 4 and 5 give the calculated and observed values for comparison. The boiling point curves for the first three systems show neither maximum nor minimum, but for the system acetone-chloroform this curve shows a maximum at composition 0.345 mol acetone (total pressure 760 mm.), and for the system alcohol-water a minimum at composition 0.904 mol alcohol.

Table VI—Comparison of Observed and Calculated Compositions of the Equilibrium Vapor

MOLS BENZENE IN EQUILIBRIUM VAPOR				
Mols benzene in liquid	Calcd. from $P'_B = P_{B_0} X_B$	Calcd. from $P''_B = P - P'_T$	Calcd. from $P_B = P'_B X_B + P''_B X_T$	Obsd. ^a
System: Benzene-Toluene at 750 Mm.				
0.2	0.377	0.384	0.382	0.372
0.4	0.628	0.622	0.624	0.619
0.6	0.798	0.792	0.795	0.791
0.8	0.926	0.909	0.922	0.912
MOLS CS ₂ IN EQUILIBRIUM VAPOR				
Mols CS ₂ in liquid	Calcd. from $P'_{CS_2} = P_{CS_2} X_{CS_2}$	Calcd. from $P''_{CS_2} = P - P'_{CCl_4}$	Calcd. from $P_{CS_2} = P'_{CS_2} X_{CS_2} + P''_{CS_2} X_{CCl_4}$	Obsd. ^b
System: Carbon Disulfide-Carbon Tetrachloride at 760 Mm.				
0.111	0.236	0.267	0.263	0.266
0.258	0.454	0.500	0.488	0.495
0.532	0.718	0.768	0.743	0.747
0.757	0.872	0.899	0.878	0.878
MOLS CCl ₄ IN EQUILIBRIUM VAPOR				
Mols CCl ₄ in liquid	Calcd. from $P'_C = P_{C_0} X_C$	Calcd. from $P''_C = P - P'_B$	Calcd. from $P_C = P'_C X_C + P''_C X_B$	Obsd. ^c
System: Carbon Tetrachloride-Benzene at 760 Mm.				
0.136	0.150	0.157	0.156	0.158
0.216	0.229	0.247	0.243	0.242
0.363	0.386	0.400	0.395	0.392
0.620	0.637	0.644	0.639	0.638
0.722	0.737	0.742	0.738	0.733
MOLS ACETONE IN EQUILIBRIUM VAPOR				
Mols acetone in liquid	Calcd. from $P'_A = P_{A_0} X_A$	Calcd. from $P''_A = P - P'_{CHCl_3}$ in constant boiling mixture	Calcd. from $P_A = P'_A X_A + P''_A X_C$	Obsd. ^d
System: Acetone-Chloroform at 760 Mm.				
0.796	0.913	0.831	0.896	0.869
0.663	0.800	0.698	0.765	0.750
0.266	0.183	0.266 ^e	0.254	0.237
0.211	0.137	0.205 ^e	0.191	0.176
MOLS ALCOHOL IN EQUILIBRIUM VAPOR				
Mols alcohol in liquid	Calcd. from constant boiling mixture P'_A	Calcd. from $P''_A = P - P'_W$	Calcd. from $P_A = P'_A X_A + P''_A X_W$	Obsd. ^f
System: Alcohol-Water at 760 Mm.				
0.779	0.780	0.913	0.810	0.800
0.421	0.462	0.725	0.614	0.624
0.265	0.324	0.620	0.533	0.556
0.089	0.126	0.430	0.403	0.449

^a Rosanoff, *J. Am. Chem. Soc.*, **36**, 1999 (1914).

^b *Ibid.*, **31**, 982 (1909).

^c *Ibid.*, **31**, 971 (1909).

^d *Ibid.*, **31**, 978 (1909).

^e These values for acetone = 1—calcd. mols CHCl₃.

^f Wreuskey's results recalculated by Lewis, *THIS JOURNAL*, **12**, 496 (1920).

Agreement between observed and calculated values is excellent for the first three systems and reasonably close for the last two. It may be further commented that the values given as "observed" are by no means necessarily the true values. For example, the accurate analysis of mixtures of benzene and toluene is not an easy matter, and the observed values given may differ from the truth to an extent greater than the differences between observed and calculated compositions. This is not always the case and does not mean that the values calculated are in exact agreement with the truth, but merely indicates that observed values should not be accepted implicitly. It is interesting to note that the agreement is exceedingly close for the system benzene-carbon

tetrachloride—that is, for one composed of substances whose specific physical properties are so different as to allow accurate analysis.

In general, it may be said that the literature does not afford an abundance of data allowing the construction of complete families of Dühring lines. Fewer experimentally established equilibrium diagrams are available. Further work needs to be done before the value of the method outlined above can be fully determined.

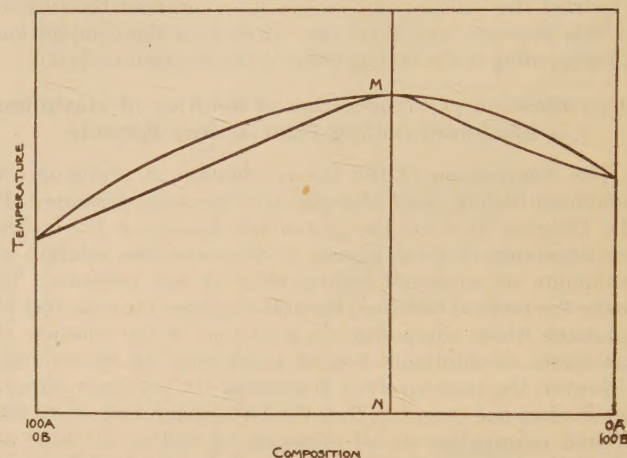


Figure 11—Equilibrium Diagram of a Binary System Showing a Maximum Boiling Point

Summary

1—A modified apparatus suitable for the measurement of the boiling points of organic solutions has been described.

2—The vapor pressures of *n*-hexane, *n*-heptane, *n*-octane, and solutions of hexane-heptane, hexane-octane, and heptane-octane have been determined within the limits in which the substance or solutions showed the same vapor pressure as water in the temperature interval 50° to 100° C.

3—Dühring's rule has been shown to hold for solutions each component of which exerts an appreciable vapor pressure. The range investigated was 92.3 to 760 mm. pressure, corresponding to boiling points of water between 50° and 100° C. Heretofore Dühring's rule has been recognized as applicable to pure substances, or to solutions from which the solvent alone was volatile. Dühring's rule has been extended to include all types of binary systems, including those whose components are partly or completely soluble and whose boiling point curves show a maximum, a minimum, or neither maximum nor minimum. The law also holds for the ternary solutions investigated.

4—The Dühring lines afford a rapid method for constructing vapor pressure curves, as only two boiling point determinations are necessary for the construction of a line from which a vapor pressure curve is drawn.

5—A method for the construction of equilibrium diagrams at any pressure, from the Dühring data, has been formulated and the equilibrium diagrams for hexane-heptane, hexane-octane, and heptane-octane have been drawn. Agreement between observed and calculated values is excellent for all systems investigated that have vapor pressure curves showing neither maximum nor minimum. Only two systems of this type have been studied and, although observed and calculated diagrams are in fair agreement, many more systems of this type must be investigated before conclusions should be drawn.

6—The utility of the Dühring data in connection with the analysis of solutions, determination of composition of the solution of minimum or maximum boiling point at any pressure, and calculation of latent heats has been indicated.

